

Conductivity and Viscosity of Dilute Solutions
of Lithium Nitrate and Cadmium Iodide in
Binary and Ternary Mixtures of Acetone with
Methyl Alcohol, Ethyl Alcohol and Water.

By

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The work of Jones with Lindsay¹⁾, Carroll²⁾, Bingham³⁾, McMaster⁴⁾ and Veazey⁵⁾, bearing upon the relations existing between conductivity and viscosity of solutions of electrolytes in mixed solvents, has shown that, with a large number of compounds, in binary mixtures of methyl alcohol, ethyl alcohol, acetone and water, the curves representing fluidity (the reciprocal of viscosity) and molecular conductivity have approximately the same form, whether the curves correspond with the rule of mixtures, or pass through maxima or minima as the composition of the solvent mixture is changed. The investigations had to do with about twelve different electrolytes, and measurements were made at 0° and 25°.

The relations existing between conductivity and viscosity have been the subjects of investigation by many others.

G. Wiedemann⁶⁾ showed that the conductivity of copper sulphate in water varies inversely as the coefficient of viscosity, and directly as the concentration.

Stephan⁷⁾ expressed his view that each ion of a dissolved electrolyte carries with it an atmosphere of the solvent molecules, so that the

¹⁾ Amer. Chem. Journ. **28**, 329 (1902); Zeitschr. f. physik. Chemie **56**, 129 (1906).

²⁾ Amer. Chem. Journ. **32**, 521 (1904); Zeitschr. f. physik. Chemie **56**, 129 (1906).

³⁾ Amer. Chem. Journ. **34**, 481 (1905); Zeitschr. f. physik. Chemie **57**, 193 (1907).

⁴⁾ Amer. Chem. Journ. **36**, 325 (1906); Zeitschr. f. physik. Chemie **57**, 257 (1907).

⁵⁾ Zeitschr. f. physik. Chemie **61**, 641 (1908); **62**, 44 (1908).

⁶⁾ Pogg. Ann. **99**, 229 (1856).

⁷⁾ Wied. Ann. **17**, 673 (1882).

resistance to the movement of the ion during the passage of an electric current is, in each case, due to friction of solvent molecules with each other. He concluded that, in alcohol-water mixtures, the conductivity at great dilutions is to be obtained by multiplication of the conductivity in water by a factor which depends only upon the percentage of alcohol, and not upon the nature of the electrolyte; also that molecular conductivity is proportional to fluidity until the proportion of alcohol becomes greater than about 50 per cent., when the conductivity is less than would be expected.

Grossmann¹⁾ concluded that the product of the molecular conductivity of a given electrolyte with the viscosity of its solutions, is constant and is independent of temperature.

Arrhenius²⁾ noted the dependence of conductivity upon fluidity, but showed that the nature of the electrolyte must also condition the conductivity in dilute solutions, since otherwise all completely dissociated electrolytes would have the same molecular conductivity in a given solvent.

Völlmer³⁾ showed that, with a large number of electrolytes, the temperature coefficients of conductivity and of fluidity are identical.

Cohen⁴⁾ studied conductivities in mixtures of water and alcohol, and decided that, for a given electrolyte in a given solvent mixture, the molecular conductivity bears a constant ratio to that for the same concentration of the electrolyte in water; the constant being independent of the concentration. This holds also for molecular conductivity at infinite dilution. This conclusion is similar to that reached by Stephan.

Sutherland⁵⁾ stated that the degree of dissociation of a dissolved electrolyte is related to both conductivity and viscosity, thus:

$$\alpha_v = \frac{\mu_v}{\mu_\infty} \cdot \frac{\eta}{\eta_\infty}.$$

Walden⁶⁾ determined the viscosity and maximum molecular conductivity of tetraethyl ammonium iodide in water, as well as in about thirty different organic solvents, and showed that, at both 0° and 25°, the product of viscosity coefficient and maximum molecular conductivity is constant, and that the value of the constant is the same for

¹⁾ Wied. Ann. **18**, 119 (1883).

²⁾ Zeitschr. f. physik. Chemie **9**, 487 (1892).

³⁾ Wied. Ann. **52**, 328 (1894).

⁴⁾ Zeitschr. f. physik. Chemie **25**, 1 (1898).

⁵⁾ Phil. Mag. [6] **3**, 167 (1902).

⁶⁾ Zeitschr. f. physik. Chemie **55**, 207 (1906).

both temperatures and for all of the solvents examined, with the exceptions of water and glycol. The value for water was found to be 1.00, that for glycol 1.32 and the mean for all of the other solvents examined 0.700. He remarked that water and glycol seem to stand in distinct classes, as is the case with regard to many other properties. Having this relation in mind, he thought it possible to calculate the maximum molecular conductivity from the known constant and the viscosity coefficient. In the cases studied by Walden, he found the temperature coefficients of conductivity and of fluidity to be the same.

Arndt¹⁾ referred to the work of others upon this subject and stated that all of the results pointed to the rule that conductivity and viscosity vary inversely. He worked with fused mixtures of sodium metaphosphate and boron trioxide, and found this rule to hold above 900°.

In the work of Jones with Bingham²⁾ and with McMaster³⁾, certain exceptions to this general relation were found. Lithium bromide, lithium nitrate, cobalt chloride and calcium nitrate, in all solvent mixtures containing acetone as one of the components, gave molecular conductivity curves which differed from the fluidity curves in a striking manner. The conductivity values for pure acetone, and for those solvent mixtures containing a large proportion of acetone, were abnormally low, — so much so that when curves were drawn to represent, respectively, molecular conductivity and fluidity, for changing composition of the solvent mixtures, in some cases maxima appeared in the molecular conductivity curves for those solutions whose fluidity curves showed minima. Further examination of the conductivities in acetone showed that, instead of conforming with Ostwald's, or any other known dilution law, they first increased very slowly with dilution, and later quite rapidly.

Although these exceptions were overlooked by Arndt in his discussion, they seemed to us to be sufficient to destroy the force of any proposed law which correlates conductivity and viscosity, unless some explanation could be found for the anomalous behavior of solutions of these salts in acetone. This investigation was undertaken in order, if possible, to find the explanation. If, in general, solvents having a small viscosity coefficient should give solutions of high molecular conductivity with electrolytes which are largely dissociated in them, it is evident that solutions in acetone should exhibit much higher conductivity than solutions in ethyl alcohol, methyl alcohol or water, since the viscosity

¹⁾ Z. f. Elektroch. **13**, 809 (1907).

²⁾ Loc. cit.

³⁾ Loc. cit.

coefficient of acetone is much smaller than that of any of the other three solvents. The fact that the above named salts show abnormally low conductivities in acetone, thus points to the probability of a relatively small ionic concentration. If we consider first the way in which the conductivities increase with increasing dilution, it will be noticed that the first slow increase in molecular conductivity suggests the case of a dilute solution of a nearly completely dissociated salt, while the later rapid increase is what would occur if more of the salt were continually added. This is what might be expected if the salt in the more concentrated solutions were associated to a greater or less extent. This would result in a small initial concentration of single molecules, which, existing in equilibrium with the ionized portion, might themselves obey, at least approximately, one of the dilution laws. Association would become less as more of the solvent were added, resulting in an increase in the number of single molecules, and, subsequently, of ions in the solution.

In 1902 Jones¹⁾ showed that certain salts have abnormally high molecular weights in acetone solutions, although the same solutions conduct the electric current to a considerable extent. He pointed out the fact that this is not inconsistent with Arrhenius' theory of electrolytic dissociation, since it is quite conceivable that association and dissociation may occur in the same solution. It may be remarked that this is known to be the case, for instance, with many homogeneous liquids, such as water. The salts examined by Jones and found to have molecular weights above the normal were cadmium iodide and ammonium sulphocyanate, both of which Dutoit and Friderich²⁾ had previously described as having normal molecular weights in acetone. If the above noted abnormal conductivities are to be explained by assuming association of the electrolyte, it should be possible, by attaining sufficiently great dilution, to break down these associated molecules into single molecules, and, subsequently, into ions; in which case the molecular conductivity might reach a value in accord with the rule which has been established in practically all other cases which have been tested, namely, that molecular conductivity is inversely proportional to viscosity. The curves representing molecular conductivity and fluidity, respectively, would then assume similar forms, minima in the one corresponding to minima in the other, etc.

¹⁾ Amer. Chem. Journ. **27**, 16 (1902).

²⁾ Bull. Soc. Chim. [3] **19**, 334 (1898).

An effort has been made to determine the conductivities of the solutions in question at high dilutions, approaching the region of complete dissociation. We can, at present, see no reason why there should be any constant relation between molecular conductivity and viscosity in different solvents, until this point is reached, bearing in mind the widely differing degrees of dissociation existing in solutions of the same concentration in different solvents. In very dilute solutions the difference between the viscosity of the solution and that of the solvent is generally much less than the experimental error, hence we have directly compared our values for the conductivity of the solution with those for the viscosity of the solvent.

The questions for which we have sought the answer are, then, the following:

1. Will those salts that have, at ordinary concentrations, abnormally low values for molecular conductivity possess, when completely dissociated, values which are inversely proportional to the coefficient of viscosity?

2. If so, is the product of molecular conductivity and viscosity constant for mixed solvents and at different temperatures?

3. Is the value of the constant the same for different electrolytes?

4. Are the abnormal conductivities in acetone and mixtures of acetone with other solvents due to association of the salt?

Experimental.

The determination of conductivity in very dilute solutions is attended with considerable difficulty. Dutoit and Levier¹⁾, and Dutoit²⁾, commenting upon the lack of agreement between conductivity values in acetone, as obtained by different investigators, attributed the differences chiefly to the use of platinized electrodes, to the action of light, and to the use of impure solvents. Cohen³⁾ had already noticed that electrodes which are coated with platinum black cause changes in the solutions, resulting in fictitious conductivity values; and he supposed this to be due to catalytic action of the platinum black. Dutoit and Levier also showed that such electrodes gave rise to errors, through adsorption of the dissolved substance. They also observed that the action of light upon acetone solutions causes a decrease in the conductivity,

¹⁾ Journ. Chim. Phys. **3**, 435 (1905).

²⁾ Z. f. Elektroch. **12**, 642 (1906).

³⁾ Loc. cit.

this change being reversed if the solution is subsequently placed in the dark.

In working with very dilute solutions it becomes necessary, either to make comparatively large amounts of each solution by direct weighing of the electrolyte, or to obtain the highly dilute solution by successive additions of solvent to the more concentrated solutions. The first method becomes impracticable when using solvents which are relatively difficult to prepare in the pure state. The second method introduces the error due to the large number of volume measurements which are necessarily made. We have, however, followed the latter method, making each solution from the one next higher in concentration.

Apparatus.

In making conductivity measurements Kohlrausch's method was used, the Wheatstone bridge, induction coil, resistance coils and telephone being made by Leeds and Company, of Philadelphia. The resistance coils were guaranteed to be accurate to within 0.04 percent. For high resistances, two sets of coils were placed in series, giving a total available resistance of 42,000 ohms. The bridge wire was calibrated by the method of Strouhal and Barus¹⁾. For compensating the electrostatic capacity of the conductivity cells when measuring high resistances a condenser was used, consisting of two brass plates, sliding over each other and separated by a thin sheet of paraffined paper. The conductivity cells were those described by Jones and Bingham²⁾, and the resistance capacity was determined by the use of 0.02 normal and 0.002 normal potassium chloride solutions, 129.7, the value given by Ostwald³⁾, being taken as the molecular conductivity of the 0.02 normal solution. The electrodes were platinized before using, by electrolysis of a dilute solution of platinum chloride in the cell, after which they were heated in the flame of a blast-lamp until whitened. After using a given solution, the cell was thoroughly washed out and allowed to stand filled with distilled water for at least a day; it was then dried by means of alcohol. We satisfied ourselves, by repeated tests, that this method of drying did not produce acid on the electrodes. Measurements were made at 0° and 25°. The thermometers were graduated in 0.2° intervals and were compared with a thermometer which was certified by the Reichsanstalt.

¹⁾ Wied. Ann. 10, 326 (1880).

²⁾ Amer. Chem. Journ. 34, 493 (1905).

³⁾ Lehrbuch, 2. Aufl., S. 732.

Viscosity measurements were made by means of a modified form of the Ostwald viscometer¹⁾. The modification has been described by Jones and Veazey²⁾. Viscosity was calculated from the formula:

$$\eta = \eta_0 \cdot \frac{ST}{S_0 T_0}$$

in which η is the viscosity coefficient for the fluid in question, η_0 is the viscosity coefficient for water at the temperature at which the experiment is being carried out, S is the specific gravity of the solvent or solution, T is the time of flow of the solvent or solution, S_0 is the specific gravity of water at the given temperature, and T_0 is the time of flow for water. Fluidity was calculated from the formula:

$$\text{Fluidity} = \Phi = \frac{1}{\eta}.$$

The viscosity coefficients for water which were used in the calculations, are those taken from the researches of Thorpe and Roger³⁾. Specific gravities were determined by the use of the picnometer described by Jones and Veazey. The viscometers and picnometers were made for us by Eimer and Amend of New York.

Burettes and graduated flasks were calibrated by direct weighing of distilled water, on the basis of the true liter, and corrected to use at 20°. Pipettes were not used in any part of the work.

Solvents.

Water was purified by the method of Jones and Mackay⁴⁾, ordinary distilled water being twice redistilled from chromic acid and once from barium hydroxide. The stills and bottles were protected from the entrance of carbon dioxide by a tube of soda lime. The average specific conductivity of the purified water was 1.2×10^{-6} at 0°.

Methyl alcohol was prepared by boiling over lime and subsequent distillation into a bottle containing fresh lime, where it was allowed to stand for several weeks. It was redistilled immediately before using, and its average specific conductivity was 1×10^{-6} at 0°.

Ethyl alcohol was prepared in the same manner as methyl alcohol. The average specific conductivity at 0° was 5×10^{-7} .

Acetone was allowed to stand for a month or more over fused

¹⁾ Physik.-chemische Messungen, 2. Aufl. S. 259.

²⁾ Zeitschr. f. physik. Chemie **61**, 641 (1908).

³⁾ Phil. Trans. **185** (A), 307 (1894).

⁴⁾ Zeitschr. f. physik. Chemie **22**, 237 (1897).

calcium chloride, and was distilled immediately before using. Our experience with acetone was quite different from that of Dutoit¹⁾, in that we found that either acetone or solutions in acetone increased in conductivity very decidedly when exposed to sunlight or even fairly bright diffused light. After distillation, therefore, the acetone was kept in the dark except when being used. It is believed that any error due to impurities in the acetone, has been small in most cases, since acetone was obtained having a specific conductivity as low as 0.57×10^{-7} reciprocal Siemens units at 0° , and 0.75×10^{-7} at 25° . Dutoit and Levier stated that Benz²⁾ obtained acetone, having a specific conductivity of 0.23×10^{-7} reciprocal Siemens units at 18° , this being the lowest of which we have found any record.

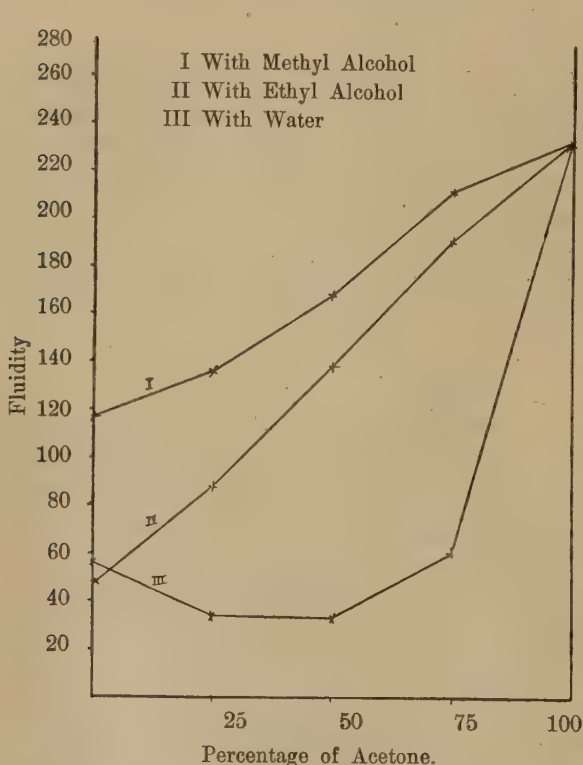


Fig. 1. Fluidity of Acetone Mixtures at 0° .

Solutions.

In all cases conductivity measurements were made with solutions from solvents which were distilled on the same or the preceding day. Solvents and solutions were kept in bottles of Jena glass. In mixing solvents and in making solutions, they were placed in a 20° bath for some time before diluting to the mark on the flask.

In designating mixed solvents, percentage by volume is understood.

An examination of the published viscosity data for mixed solvents will show that there are slight differences between the values given by different investigators,

¹⁾ Loc. cit.

²⁾ Dissertation, Lausanne 1905.

although those given by any one person are generally consistent among themselves. It is probable that such discrepancies are caused chiefly by differences in the amount and kind of unavoidable impurities in the solvents. For this reason we have determined the viscosity of all of our solvents, and the data given in table 1 are those which have been obtained in this investigation. Figures 1 and 2 are drawn from these data.

In table 1, the symbols have the following significance: η_0° is the coefficient of viscosity at 0° , η_{25}° that at 25° , Φ_0° the fluidity at 0° , and Φ_{25}° that at 25° . The temperature coefficient of fluidity is the change in fluidity per degree, divided by the fluidity at 0° .

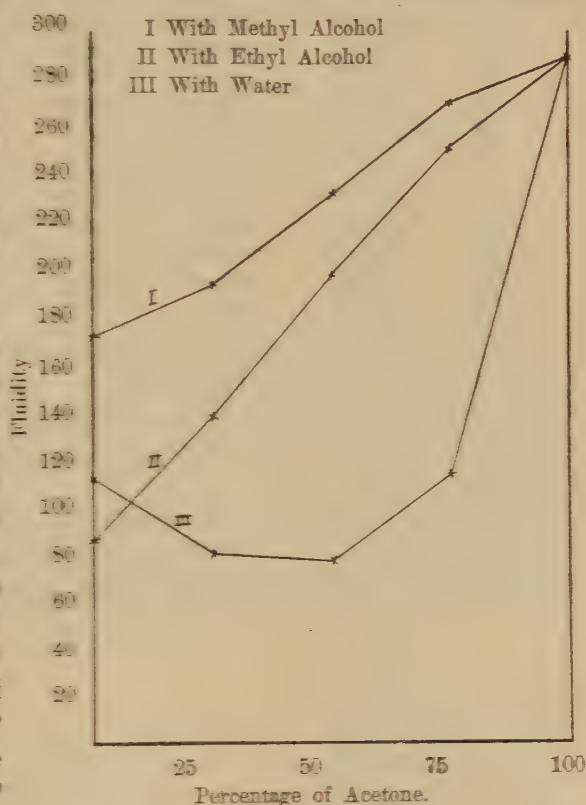


Fig. 2. Fluidity of Acetone Mixtures at 25° .

Table 1.

Viscosity and Fluidity of Acetone Mixtures at 0° and 25° .

% Acetone	η_0°	η_{25}°	Φ_0°	Φ_{25}°	Temp. Coeff.
With Methyl Alcohol.					
0	0.00567	0.00583	116.71	171.60	0.0176
25	0.00574	0.00517	136.22	192.24	0.0167
50	0.00596	0.00433	167.76	231.01	0.0151
75	0.00471	0.00370	212.29	270.12	0.0109
100	0.00422	0.00346	238.21	288.95	0.0096

% Acetone	η 0°	η 25°	Φ 0°	Φ 25°	Temp. Coeff.
		With Ethyl Alcohol.			
0	0.02103	0.01180	47.56	84.74	0.0313
25	0.01131	0.00726	88.43	137.77	0.0223
50	0.00725	0.00506	137.92	197.48	0.0173
75	0.00522	0.00398	191.54	251.29	0.0125
100	0.00429	0.00346	233.21	288.95	0.0096
		With Water.			
0	0.01778	0.00891	56.24	112.30	0.0399
25	0.02908	0.01250	34.38	79.89	0.0529
50	0.03005	0.01305	33.28	76.63	0.0521
75	0.01659	0.00885	60.29	112.97	0.0349
100	0.00429	0.00346	233.21	288.95	0.0096

In the conductivity tables, molecular conductivities are indicated, and V is the number of liters of solution containing a gram-molecule of the electrolyte. The temperature coefficient of conductivity is the change in molecular conductivity per degree, divided by the molecular conductivity at 0°.

The first compound which we studied in this connection was lithium nitrate, and the sample used was Kahlbaum's preparation, which after testing was dried to constant weight at 150°.

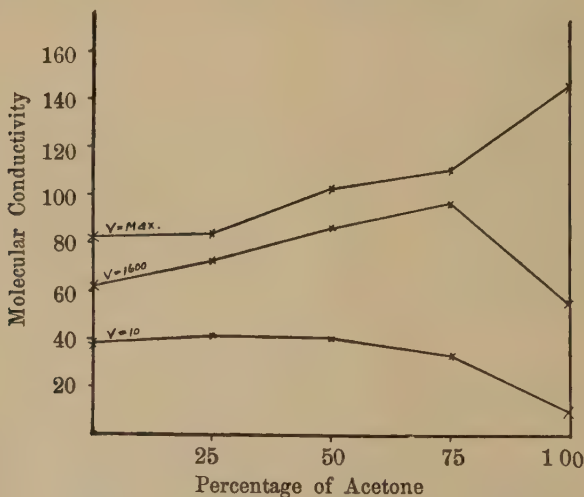


Fig. 3. Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 0°.

The conductivity of lithium nitrate in mixtures of acetone with methyl alcohol, ethyl alcohol, and water, respectively, was determined by Jones and Bingham¹⁾, using solutions whose concentration varied

¹⁾ Loc. cit.

from $V = 10$ to $V = 1600$. The results are as already indicated, namely, that the form of the curves representing molecular conduc-

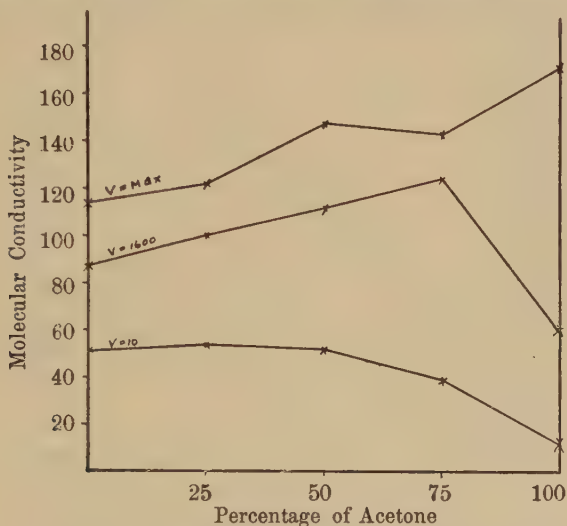


Fig. 4. Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol at 25°.

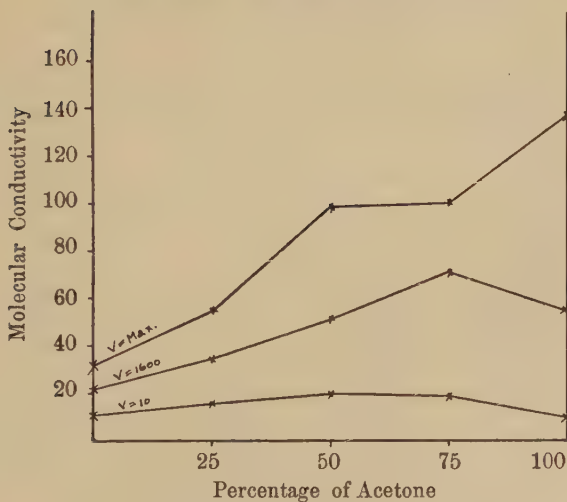


Fig. 5. Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 0°.

tivity for different percentages of acetone was different from that of the fluidity curves, in that conductivities in acetone were decidedly less than normal, and that no known dilution law would apply to the

more concentrated solutions. We have used the same solvents and mixtures of solvents, and have measured the conductivities at dilutions as

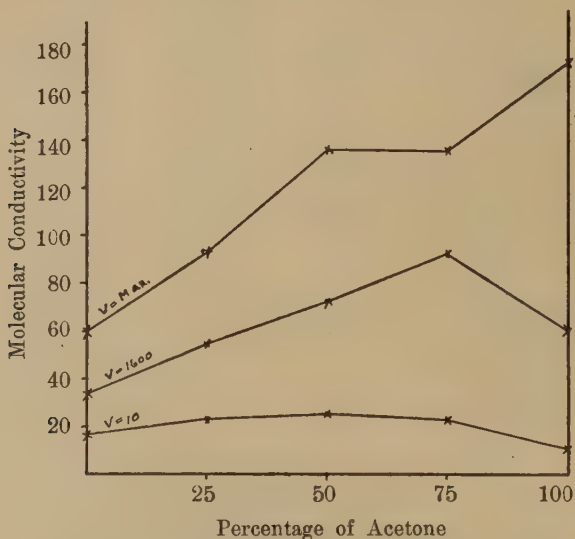


Fig. 6. Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol at 25°.

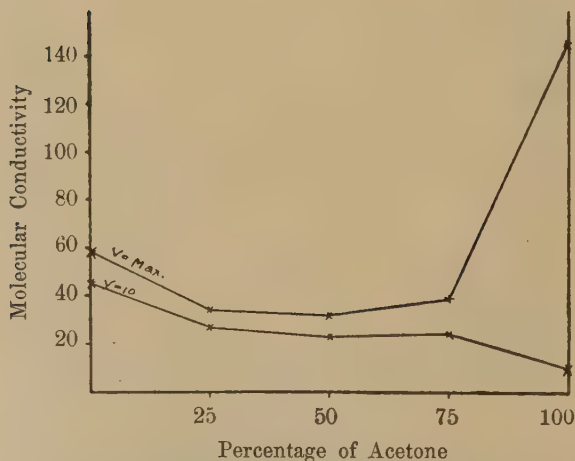


Fig. 7. Conductivity of Lithium Nitrate in Mixtures of Acetone and Water at 0°.

high as was possible with any fair degree of accuracy, considering the conductivity of the solvent. The results are shown in tables 2 to 5 and

in figures 3 to 8, inclusive. In the figures, the curves for $V = 10$ and $V = 1600$ are drawn from the data of Jones and Bingham, and

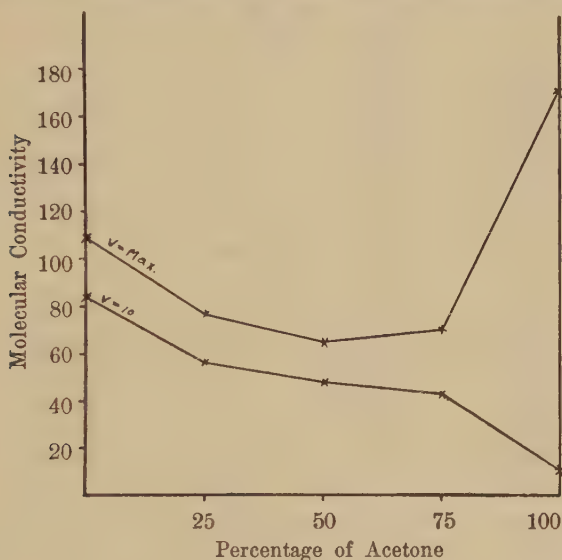


Fig. 8. Conductivity of Lithium Nitrate in Mixtures of Acetone and Water at 25°.

are given here in order to show the abnormality produced by acetone as a solvent, and the striking change in the conductivity as the dilution increases.

Table 2.

Conductivity of Lithium Nitrate in Mixtures of Acetone and Methyl Alcohol.

At 0°.

V	% Acetone.				
	0%	25%	50%	75%	100%
2 500	63.4	69.6	87.0	96.8	61.0
5 000	66.1	71.8	91.5	101.5	76.9
10 000	68.1	78.8	99.4	103.5	94.1
30 000	81.6	84.3	103.0	110.9	—
50 000	83.0	83.8	—	—	129.8
100 000	—	—	—	—	146.5

At 25°.

V	0%	25%	50%	75%	100%
2 500	88.6	97.2	122.7	124.5	65.9
5 000	92.5	100.1	132.5	131.1	85.7
10 000	94.3	107.9	144.0	133.7	105.1
30 000	113.2	121.5	138.0	142.6	—
50 000	114.0	114.5	—	—	153.6
100 000	—	—	—	—	171.8

Table 3.

Conductivity of Lithium Nitrate in Mixtures of Acetone and Ethyl Alcohol.

V	At 0°.				
	% Acetone.				
	0%	25%	50%	75%	100%
2 500	22.2	35.9	53.0	—	61.0
5 000	22.7	38.0	56.1	79.8	76.9
10 000	24.1	38.7	57.3	81.6	94.1
30 000	28.1	—	—	80.6	—
50 000	27.2	43.4	64.9	79.7	129.8
100 000	32.0	55.0	71.9	100.0	146.5
200 000	—	—	99.3	—	—
At 25°.					
2 500	37.4	55.5	74.5	97.3	65.9
5 000	38.3	58.1	79.3	105.2	85.7
10 000	40.0	59.4	83.3	109.0	105.1
30 000	48.0	—	—	106.5	—
50 000	44.7?	68.5	93.4	112.8	153.6
100 000	60.1	93.0	105.1	135.4	171.8
200 000	—	—	136.1	—	—

Table 4.

Conductivity of Lithium Nitrate in Mixtures of Acetone and Water.

V	At 0°.				
	% Acetone.				
	0%	25%	50%	75%	100%
2 500	56.9	34.1	29.9	37.2	61.0
5 000	58.4	34.2	31.4	37.6	76.9
10 000	58.5	33.5	31.8	38.7	94.1
50 000	—	—	—	—	129.8
100 000	—	—	—	—	146.5
At 25°.					
2 500	104.6	73.4	61.6	66.7	65.9
5 000	108.3	74.7	64.4	69.3	85.7
10 000	108.7	76.3	64.8	69.6	105.1
50 000	—	—	—	—	153.6
100 000	—	—	—	—	171.8

Table 5.

Temperature Coefficients of Conductivity of Lithium Nitrate.

V	% Acetone.				
	0%	25%	50%	75%	100%
In Acetone and Methyl Alcohol.					
2 500	0.0159	0.0159	0.0164	0.0115	0.0032
5 000	0.0159	0.0157	0.0179	0.0116	0.0046
10 000	0.0153	0.0147	0.0182	0.0117	0.0047
30 000	0.0155	0.0176	0.0136	0.0114	—
50 000	0.0149	0.0146	—	—	0.0073
100 000	—	—	—	—	0.0070

V	0%	25%	50%	75%	100%
In Acetone and Ethyl Alcohol.					
2 500	0.0274	0.0218	0.0162	—	See Above
5 000	0.0275	0.0212	0.0166	0.0127	"
10 000	0.0264	0.0205	0.0181	0.0134	"
30 000	0.0283	—	—	0.0128	"
50 000	0.0257	0.0231	0.0175	0.0161	"
100 000	0.0351	0.0276	0.0184	0.0142	"
In Acetone and Water.					
2 500	0.0335	0.0461	0.0426	0.0317	See Above
5 000	0.0342	0.0473	0.0420	0.0337	"
10 000	0.0343	0.0511	0.0415	0.0319	"

In the solutions in pure water and in pure acetone it would seem that complete dissociation has been very nearly attained. In water solution the value for μ_{∞} at 18°, calculated from the law of Kohlrausch and by use of the constants for the ions of lithium nitrate as given by him¹⁾, is 95. The corresponding value, calculated from our highest conductivity at 0°, by use of the temperature coefficient, is 94. In the solutions other than in water and acetone complete dissociation has not been reached, but we have approached it closely enough that the properties of the completely dissociated solution may be predicted. The conductivity curves have assumed nearly the same form as the fluidity curves for the solvents.

In order to test the applicability of Ostwald's dilution law, the values of $K = \frac{\alpha^2}{(1 - \alpha)\nu}$ have been calculated for the solutions of lithium nitrate in acetone, from all available data. In table 6 the values for μ_v from $V = 10$ to $V = 1600$, inclusive, are taken from the paper of Jones and Bingham. From this point the values are those which have been obtained in this investigation.

Table 6.

Ionization Constant for Lithium Nitrate in Acetone.

At 0°.				At 25°.			
V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$
10	0.541	1 600	0.168	10	0.670	1 600	0.130
50	0.235	2 500	0.120	50	0.195	2 500	0.096
100	0.198	5 000	0.117	100	0.156	5 000	0.098
200	0.186	10 000	0.116	200	0.134	10 000	0.096
400	0.165	50 000	0.145	400	0.115	50 000	0.147
800	0.179			800	0.126		

¹⁾ Sitzungsber. d. K. Preuss. Akad. d. Wiss. Math. Kl. 1904, 574 u. 582.

It will be seen that K becomes practically constant at $V = 200$, for solutions at both 0° and 25° ; which would indicate that the highest value for μ_v , that obtained at $V = 100.000$, is not far from the maximum molecular conductivity. The fact that K decreases rapidly at first, may be explained on the general ground that Ostwald's dilution law is not applicable to solutions of strong electrolytes, or upon the assumption of polymerization of the electrolyte. It will appear later that there is reason for the latter view.

In table 7 is given the calculated product of viscosity and molecular conductivity for all of the solutions. In these calculations we have used, in each case, the viscosity of the solvent, which is practically identical with that of the dilute solution, and have taken for μ_v the highest value which has been obtained in this work.

Table 7.

$\eta \cdot \mu_v$ for Lithium Nitrate in Mixed Solvents.

% Acetone	$\mu_v 0^\circ$	$\eta 0^\circ$	$\eta \cdot \mu_v$	$\mu_v 25^\circ$	$\eta 25^\circ$	$\eta \cdot \mu_v$
In Acetone and Methyl Alcohol.						
0	83	0.0086	0.69	114	0.0058	0.65
25	84	0.0073	0.61	122	0.0052	0.63
50	103	0.0060	0.62	144	0.0043	0.62
75	111	0.0047	0.52	143	0.0037	0.53
100	146	0.0043	0.63	172	0.0035	0.60
In Acetone and Ethyl Alcohol.						
0	32	0.0210	0.67	60	0.0118	0.71
25	55	0.0113	0.62	93	0.0073	0.71
50	100	0.0072	0.72	136	0.0051	0.69
75	100	0.0052	0.52	135	0.0040	0.54
100	146	0.0043	0.63	172	0.0035	0.60
In Acetone and Water.						
0	58	0.0178	1.03	108	0.0089	0.96
25	34	0.0291	0.99	76	0.0125	0.95
50	32	0.0300	0.96	65	0.0131	0.85
75	39	0.0166	0.65	70	0.0088	0.62
100	146	0.0043	0.63	172	0.0035	0.60

The product of viscosity and molecular conductivity is seen to be nearly a constant, for mixtures of acetone with methyl alcohol and with ethyl alcohol. This constant is independent of temperature and its value is nearly 0.70, — the value found by Walden for tetraethyl ammonium iodide in a large number of organic solvents. For mixtures of acetone with water, the product varies between about 1.00, the value for water, and about 0.60, that for acetone. The product for water is

also shown to be the same as Walden's constant for water solutions. It is probable that, if complete dissociation could have been obtained in acetone, the product for this solution would have been found to be nearly 0.70, and that the product for mixtures of acetone and water would conform to the rule of mixtures. We have no explanation to offer for the fact that water differs so strikingly from the organic solvents, with respect to the numerical value of the product of maximum molecular conductivity and viscosity.

In order to test the assumption that the low conductivity shown by ordinary solutions of lithium nitrate in acetone is due to association of the salt, the molecular weight of lithium nitrate in acetone was de-

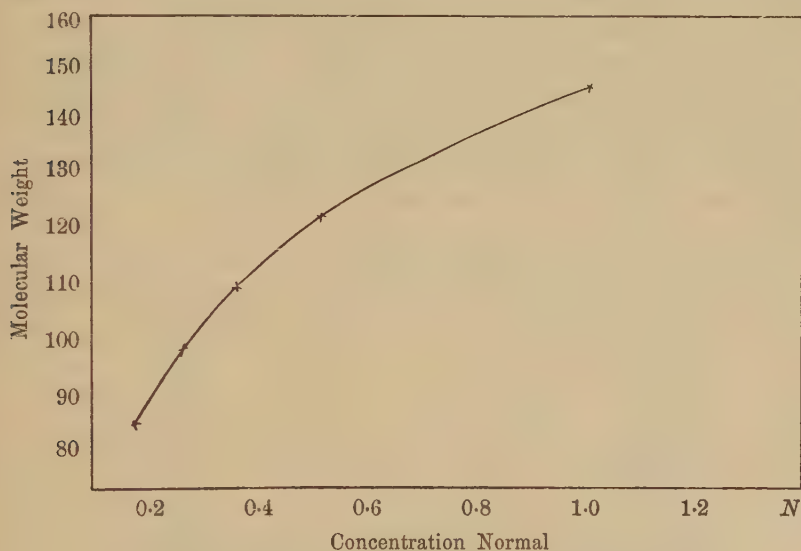


Fig. 9. Molecular Weight of Lithium Nitrate in Acetone.

termined by the boiling-point method. The apparatus used was the apparatus, designed by Jones¹⁾, the thermometer being the Beckmann instrument, graduated to 0.01°. The boiling-point constant for acetone was taken as 17.25, which is that found in a redetermination by Jones²⁾. The usual corrections were made for changes in barometric pressure. The results are shown in table 8, and the molecular weights are plotted against concentrations in figure 9.

¹⁾ Amer. Chem. Journ. **19**, 581 (1897); Zeitschr. f. physik. Chemie **31**, 119 (1899).

²⁾ Amer. Chem. Journ. **27**, 16 (1902).

Table 8.

Molecular Weight of Lithium Nitrate in Acetone.

Acetone Grams	LiNO_3 Grams	Concentration Normal	<i>B. P. Rise</i> Degrees	Molecular Weight
58.07	0.3625	0.09	0.130°	83.1
52.74	0.7076	0.19	0.233	99.3
49.99	1.0640	0.30	0.326	112.6
46.30	2.2033	0.48	0.451	127.1
54.35	3.9229	1.05	0.805	154.7

The normal molecular weight of lithium nitrate is 69.07. The fact that, even in the most dilute solution which could be used with accuracy (0.09 N), the molecular weight is greater than this number is significant. If it be remembered that a portion of the salt is also ionized, and that the molecular weight as obtained by the boiling-point method is the average weight of associated molecules, single molecules and ions, existing simultaneously in the solution, it will readily be surmised that there must be a certain degree of association at much greater dilutions. This would explain the departure from the dilution law in those solutions in which the association has not entirely disappeared.

It has already been stated that cadmium iodide was found by Jones to be associated when dissolved in acetone. We have studied

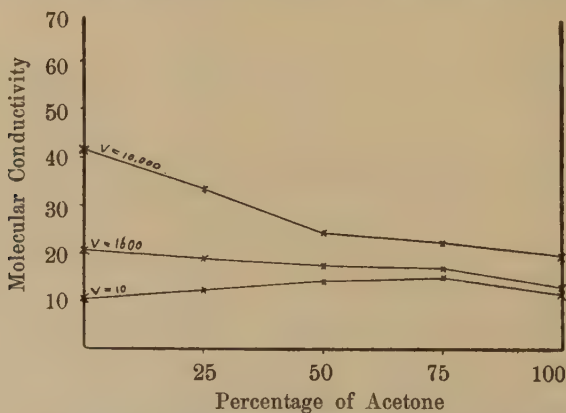


Fig. 10. Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol at 0°.

the conductivity of cadmium iodide in acetone and in binary mixtures containing acetone, in order to determine whether such solutions are analogous to those of lithium nitrate, as they should be if the proposed explanation of the peculiar behavior of the latter is correct. The results

of the conductivity measurements are shown in tables 9 to 17, and in figures 10 to 15, inclusive.

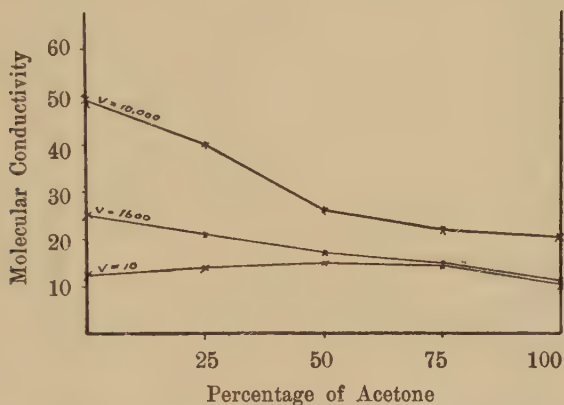


Fig. 11. Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol at 25°.

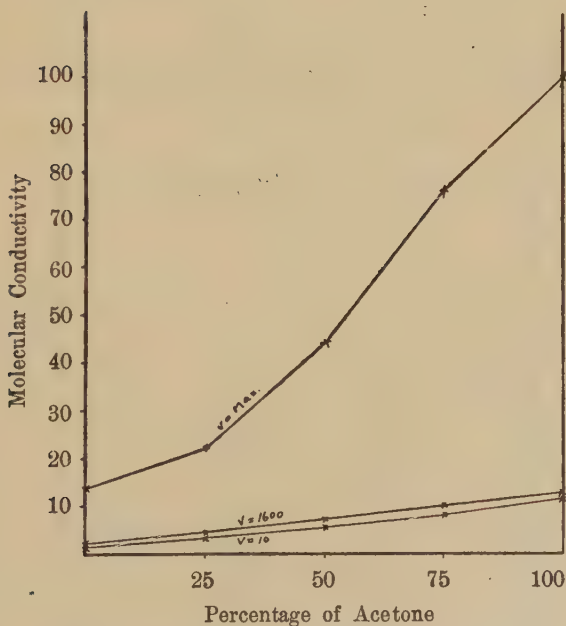


Fig. 12. Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0°.

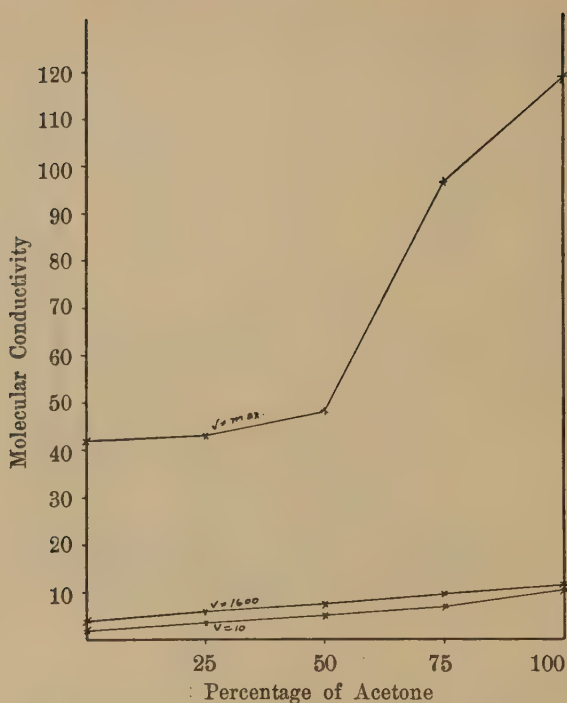


Fig. 13. Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol at 25°.

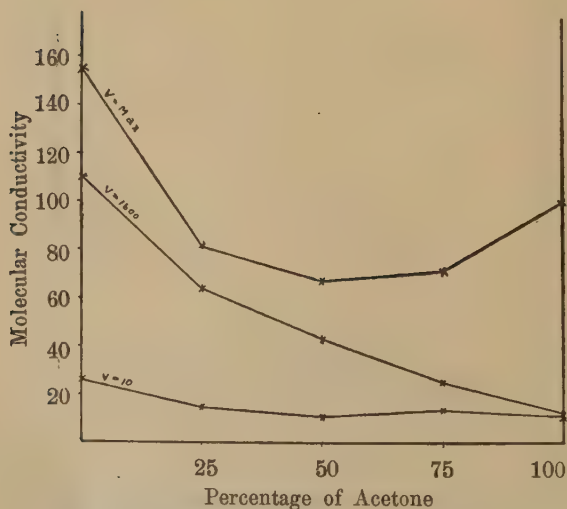


Fig. 14. Conductivity of Cadmium Iodide in Mixtures of Acetone and Water at 0°.

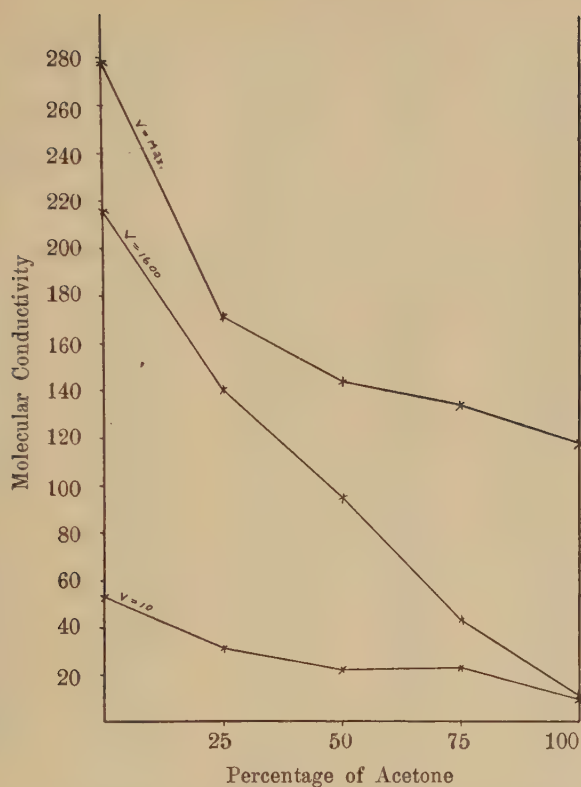


Fig. 15. Conductivity of Cadmium Iodide in Mixtures of Acetone and Water at 25°.

Table 9.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol at 0°.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	10.31	12.39	14.31	15.13	11.56
50	11.72	13.94	15.63	16.36	12.10
100	12.34	14.35	15.89	16.47	11.88
200	13.01	14.44	15.83	16.48	12.22
400	14.92	15.56	16.62	16.89	12.11
800	17.42	16.86	17.05	16.90	12.63
1 600	20.83	18.77	17.37	17.00	12.87
2 500	25.60	21.09	18.13	17.19	12.27
5 000	33.12	27.05	21.2	20.64	15.35
10 000	41.5	33.4	24.2	22.2	19.53
30 000	46.8	48.0	32.2	29.3	29.4

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
50 000	55.0	60.8	39.2	32.3	37.5
100 000	62.7	94.3	—	—	78.0
200 000	—	—	—	—	93.0
400 000	—	—	—	—	100.0

Table 10.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol at 25°.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	12.42	14.03	15.11	14.68	10.29
50	13.66	15.16	15.75	15.19	10.15
100	14.28	15.46	16.10	14.96	9.92
200	15.03	15.53	15.66	14.84	10.34
400	17.42	16.59	16.18	15.18	10.23
800	20.36	18.18	16.76	14.98	10.88
1 600	24.53	20.76	17.32	14.98	11.16
2 500	28.95	24.18	18.14	15.08	11.64
5 000	40.0	32.4	21.7	19.1	13.91
10 000	49.2	39.8	25.9	21.7	20.5
30 000	54.2	56.6	33.1	27.6	32.8
50 000	55.9	80.6	43.3	28.9	45.4
100 000	63.0	105.5	—	—	78.6
200 000	—	—	—	—	113.0
400 000	—	—	—	—	118.0

Table 11.

Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Methyl Alcohol.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	0.0082	0.0051	+ 0.0022	— 0.0011	— 0.0045
50	0.0066	0.0038	+ 0.0003	— 0.0030	— 0.0063
100	0.0063	0.0031	+ 0.0005	— 0.0036	— 0.0064
200	0.0062	0.0031	— 0.0003	— 0.0039	— 0.0061
400	0.0067	0.0026	— 0.0009	— 0.0040	— 0.0062
800	0.0066	0.0031	— 0.0007	— 0.0045	— 0.0054
1 600	0.0071	0.0064	— 0.0001	— 0.0047	— 0.0053
2 500	0.0052	0.0059	0.0000	— 0.0049	— 0.0023
5 000	0.0083	0.0078	+ 0.0009	— 0.0030	— 0.0039
10 000	0.0074	0.0077	+ 0.0028	— 0.0009	+ 0.0021
30 000	0.0063	0.0072	+ 0.0011	— 0.0023	+ 0.0046
50 000	0.0006	0.0130	+ 0.0042	— 0.0042	+ 0.0084
100 000	0.0002	0.0047	—	—	+ 0.0066
200 000	—	—	—	—	+ 0.0086
400 000	—	—	—	—	+ 0.0072

Table 12.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol at 0°.

V	0 %	% Acetone.			
		25 %	50 %	75 %	100 %
10	1.69	3.43	5.58	8.15	11.56
50	1.62	3.37	5.51	7.97	12.10
100	1.60	3.42	5.52	7.92	11.88
200	1.67	3.49	5.63	7.98	12.22
400	1.74	3.54	5.86	8.16	12.11
800	1.93	4.11	6.38	8.57	12.63
1 600	2.31	4.63	7.20	10.01	12.87
2 500	2.28	5.42	9.41	10.52	12.27
5 000	4.6	7.0	13.0	13.2	15.4
10 000	7.8	8.4	16.0	21.8	19.5
25 000	—	15.1	26.5	29.4	—
50 000	13.9	22.0	43.6	60.0	37.5
100 000	10.4	—	—	76.0	78.0
200 000	—	—	—	—	93.0
400 000	—	—	—	—	100.0

Table 13.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol at 25°.

V	0 %	% Acetone.			
		25 %	50 %	75 %	100 %
10	2.11	3.54	5.19	7.03	10.29
50	2.00	3.40	4.91	6.58	10.15
100	2.03	3.45	4.95	6.58	9.92
200	2.16	3.61	4.97	6.65	10.34
400	2.42	3.87	5.53	6.95	10.23
800	2.97	4.78	6.27	6.48	10.88
1 600	4.02	5.93	7.70	9.62	11.16
2 500	4.75	7.58	11.10	10.64	11.64
5 000	9.33	11.0	17.1	15.5	13.9
10 000	15.2	14.3	21.5	26.0	20.5
25 000	—	15.0	34.5	35.3	—
50 000	41.7	43.1	58.3	75.0	45.4
100 000	42.0	—	—	96.0	78.6
200 000	—	—	—	—	113.0
400 000	—	—	—	—	118.0

Table 14.

Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Ethyl Alcohol.

V	0 %	% Acetone.			
		25 %	50 %	75 %	100 %
10	0.0099	0.0013	— 0.0028	— 0.0055	— 0.0045
50	0.0094	0.0004	— 0.0044	— 0.0070	— 0.0063
100	0.0107	0.0004	— 0.0041	— 0.0067	— 0.0064
200	0.0118	0.0014	— 0.0047	— 0.0066	— 0.0061
400	0.0156	0.0037	— 0.0023	— 0.0059	— 0.0062

V	0 %	25 %	50 %	75 %	100 %
800	0.0215	0.0065	— 0.0007	— 0.0097	— 0.0054
1 600	0.0296	0.0112	+ 0.0028	— 0.0016	— 0.0053
2 500	0.0433	0.0157	+ 0.0072	+ 0.0005	— 0.0023
5 000	0.0413	0.0231	+ 0.0127	+ 0.0069	— 0.0039
10 000	0.0379	0.0282	+ 0.0138	+ 0.0077	+ 0.0021
25 000	—	0.0262	+ 0.0120	+ 0.0080	—
50 000	0.0800	0.0384	+ 0.0135	+ 0.0100	+ 0.0084
100 000	0.1230	—	—	+ 0.0105	+ 0.0066
200 000	—	—	—	—	+ 0.0086
400 000	—	—	—	—	+ 0.0072

Table 15.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Water at 0°.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	25.95	15.00	11.40	14.17	11.56
50	45.88	22.49	13.40	15.45	12.10
100	58.16	29.26	15.39	16.12	11.88
200	70.6	38.13	19.00	17.01	12.22
400	83.0	47.6	24.4	18.2	12.11
800	96.3	56.4	33.0	20.6	12.63
1 600	110.0	63.9	43.3	24.6	12.87
2 500	116.1	66.2	49.3	27.8	12.27
5 000	126.2	72.4	57.2	35.6	15.4
10 000	140.6	80.8	63.8	48.3	19.5
25 000	155.2	—	67.2	62.1	—
50 000	—	—	—	71.0	37.5
100 000	—	—	—	—	78.0
200 000	—	—	—	—	93.0
400 000	—	—	—	—	100.0

Table 16.

Conductivity of Cadmium Iodide in Mixtures of Acetone and Water at 25°.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	52.68	30.65	21.90	23.08	10.29
50	95.43	49.94	27.12	24.83	10.15
100	119.95	65.65	32.46	25.98	9.92
200	144.4	85.73	41.4	27.77	10.34
400	167.8	105.6	54.5	30.14	10.23
800	191.6	124.5	73.1	34.81	10.88
1 600	215.8	139.7	95.0	43.16	11.16
2 500	225.4	145.6	105.8	49.7	11.64
5 000	240.2	155.1	122.1	66.9	13.9
10 000	261.2	170.6	135.2	91.0	20.5
25 000	278.8	—	144.2	117.0	—
50 000	—	—	—	134.0	45.4

V	0%	25%	50%	75%	100%
100 000	—	—	—	—	78.6
200 000	—	—	—	—	113.0
400 000	—	—	—	—	118.0

Table 17.

Temperature Coefficients of Conductivity of Cadmium Iodide in Mixtures of Acetone and Water.

V	% Acetone.				
	0 %	25 %	50 %	75 %	100 %
10	0.0402	0.0417	0.0369	0.0251	— 0.0045
50	0.0432	0.0488	0.0409	0.0243	— 0.0063
100	0.0424	0.0484	0.0443	0.0238	— 0.0064
200	0.0418	0.0499	0.0471	0.0253	— 0.0061
400	0.0409	0.0487	0.0493	0.0261	— 0.0062
800	0.0398	0.0412	0.0486	0.0275	— 0.0054
1 600	0.0385	0.0474	0.0477	0.0302	— 0.0053
2 500	0.0376	0.0479	0.0458	0.0315	— 0.0023
5 000	0.0361	0.0456	0.0454	0.0352	— 0.0039
10 000	0.0343	0.0444	0.0447	0.0353	+ 0.0021
25 000	0.0319	—	0.0458	0.0355	—
50 000	—	—	—	0.0357	+ 0.0084
100 000	—	—	—	—	+ 0.0066
200 000	—	—	—	—	+ 0.0086
400 000	—	—	—	—	+ 0.0072

The conductivity of cadmium iodide in water has been studied by Lenz¹⁾, Grotrian²⁾, Wershoven³⁾, Zelinski and Krapivin⁴⁾, Fox⁵⁾ and Jones and Lindsay⁶⁾. Hittorf⁷⁾ determined the apparent transport numbers of the anion in solutions of different concentrations, and concluded that, in the more concentrated solutions, double molecules exist, which dissociate to Cd^{++} and CdI_4^{--} . Lenz also believed that the more concentrated solutions contain complex anions. McBain⁸⁾, on the other hand, followed a different line of argument and decided that double molecules exist, but that they dissociate to form the ions Cd^{++} and $2CdI_3^-$. The conclusion was reached that at greater dilutions these ions are also broken down into the simpler ions Cd^{++} and $3I^-$, resulting in a large increase in the molecular conductivity.

Bein⁹⁾ also studied the transport numbers of the anion of cadmium iodide at different temperatures, and showed that there is no perceptible change between 20° and 75°.

¹⁾ Mem. de St. Petersburg. [7] 30, 64 (1882). ²⁾ Wied. Ann. 18, 190 (1883).

³⁾ Zeitschr. f. physik. Chemie 5, 481 (1890). ⁴⁾ Ibid. 21, 35 (1896).

⁵⁾ Ibid. 41, 458 (1902). ⁶⁾ Amer. Chem. Journ. 28, 329 (1902).

⁷⁾ Pogg. Ann. 106, 513 (1859).

⁸⁾ Z. f. Elektroch. 11, 215 (1905).

⁹⁾ Wied. Ann. 46, 29 (1892).

From the work of Kümmel¹⁾ it is evident that the apparent transport numbers of the halogens reach their minimum values in solutions of the cadmium halides which vary in concentration from 0.01 normal to 0.002 normal. Since the abnormally large apparent transport number for the halogen is supposed to be due to the fact that cadmium migrates towards both electrodes, this accords with the idea held by Hittorf, Lenz, and McBain, that the complex anions break down with increasing dilution.

Herz and Lewy²⁾ carried out partition experiments with cadmium iodide in water and amyl alcohol, from the results of which they were led to conclude that complex ions are present in the water solution.

It is not believed that the highest values for molecular conductivity which have been obtained in the present work are, in any of the solutions except those in water, the ones corresponding to complete dissociation. McBain attributed to Zelinsky and Krapiw in the most accurate work on the conductivity of water solutions of cadmium iodide, and he regarded 278, a value calculated from their results obtained at 18°, as the correct value for the maximum molecular conductivity at 25°. This corresponds with the results of our measurements, which gave 155 at 0° and 279 at 25°. It is evident, from an inspection of the values of K , calculated from Ostwald's dilution law, that this is very close to the maximum molecular conductivity. The regular decrease in the value of K until the dilution reaches about 0.001 normal, may be attributed to the non-applicability of the dilution law of Ostwald to solutions of cadmium iodide; or may be explained by the assumption of molecular association and simple ionization, or of association accompanied by the formation of complex ions the latter being the most probable cause.

Table 18.

Ionization Constant for Cadmium Iodide in Water.

At 0°				At 25°			
V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$
10	0.338	800	0.126	10	0.425	800	0.189
50	0.257	1 600	0.108	50	0.352	1 600	0.166
100	0.223	2 500	0.089	100	0.324	2 500	0.134
200	0.194	5 000	0.071	200	0.275	5 000	0.106
400	0.190	10 000	0.092	400	0.228	10 000	0.136

The result of the work upon the molecular conductivity of cadmium iodide in acetone shows a close analogy to the case of lithium nitrate.

¹⁾ Wied. Ann. **64**, 655 (1898).

²⁾ Jahresber. Schles. Ges. f. vaterländ. Kultur, 1906, Naturw. Sek., 1—9.

There is almost no change in molecular conductivity with dilution, until a concentration of 0.0002 normal is reached. From this point the increase is quite rapid, but it has not been found possible to reach the maximum molecular conductivity, though this point has been, we believe, closely approached. The Ostwald constant, calculated for these solutions, shows a very rapid decrease until $V = 5000$, where it is constant until $V = 50000$. From this point it increases quite rapidly. The large initial value of K , with its subsequent decrease, is probably due to association of the salt. The later rise in the value of K is, no doubt, due to the fact that dissociation is not complete at $V = 400000$, so that we have used too small a value for μ_{∞} in the calculation of the dissociation at greater concentrations.

Table 19.
Ionization Constant for Cadmium Iodide in Acetone.

At 0°				At 25°			
V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$	V	$K \times 10^3$
10	1.6	2500	0.007	10	0.834	2500	0.005
50	0.33	5000	0.005	50	0.164	5000	0.003
100	0.16	10000	0.005	100	0.078	10000	0.004
200	0.08	30000	0.004	200	0.042	30000	0.004
400	0.041	50000	0.005	400	0.021	50000	0.005
800	0.012	100000	0.028	800	0.011	100000	0.014
1600	0.012	200000	0.062	1600	0.006	200000	0.108

It is thus evident that in acetone the dissociation is not complete at either temperature, although it is more nearly so at 0° than at 25°. This is to be expected from a knowledge of the temperature coefficient, which is negative below a dilution of 10000 liters, and has a very small positive value at higher dilutions. Since the change in conductivity, corresponding to a given rise in temperature, is the resultant of two factors, which are probably opposite in their effect; i. e., decrease in viscosity and probable decrease in ionization, it is seen that there must be a very large decrease in the ionization of cadmium iodide in acetone as we pass from 0° to 25°. Thus, the molecular conductivity curve for cadmium iodide in acetone-water mixtures at 0° suggests the fluidity curve for the solvents, more plainly than at 25°, and it seems probable that, could the conductivity be accurately measured at dilutions as high as 600000 or 700000 liters, the curves of molecular conductivity would become similar to those of fluidity, so that molecular conductivity and viscosity would be inversely proportional, as is the case with lithium nitrate and most other electrolytes. There is no means of knowing

what the numerical value of the product of viscosity and conductivity would be. Taking the highest conductivity which was obtained in each case, the product is irregular, as is seen in table 20.

Table 20.

$\eta \cdot \mu_v$ for Cadmium Iodide in Mixed Solvents.						
% Acetone	$\mu_v 0^\circ$	$\eta 0^\circ$	$\eta \cdot \mu_v$	$\mu_v 25^\circ$	$\eta 25^\circ$	$\eta \cdot \mu_v$
In Acetone and Methyl Alcohol.						
0	63	0.0086	0.54	63	0.0058	0.36
25	94	0.0073	0.69	105	0.0052	0.54
50	39	0.0060	0.23	43	0.0043	0.19
75	32	0.0047	0.15	29	0.0037	0.11
100	100	0.0043	0.43	118	0.0035	0.41
In Acetone and Ethyl Alcohol.						
0	14	0.0210	0.29	42	0.0118	0.50
25	22	0.0113	0.25	43	0.0073	0.31
50	44	0.0073	0.32	58	0.0051	0.30
75	76	0.0052	0.40	96	0.0040	0.38
100	100	0.0043	0.43	118	0.0035	0.41
In Acetone and Water.						
0	155	0.0178	2.76	279	0.0089	2.48
25	81	0.0291	2.36	171	0.0125	2.14
50	67	0.0301	2.02	144	0.0131	1.89
75	71	0.0166	1.18	134	0.0088	1.18
100	100	0.0043	0.43	118	0.0035	0.41

The irregularity in the value of the product of maximum conductivity and viscosity, in the case of acetone and methyl alcohol mixtures, is probably due to the fact that complete dissociation was more nearly approached in some cases than in others. The values for pure acetone and for pure methyl alcohol are, however, nearly the same, and we may expect that the curves for maximum molecular conductivity, when finally obtained, will be found to be nearly straight lines, similar to the fluidity curves for the solvents.

In the acetone and ethyl alcohol mixtures there is a fair degree of constancy in the product, and the conductivity curve is nearly the theoretical one. The acetone and water curve is also nearly the same as the fluidity curve for the solvents, and the value of the product almost exactly follows the rule of mixtures; although here again the exceptionally high value of the product for water is noticed, it being about 2.5 instead of 1.0, as in the case of lithium nitrate and tetraethylammonium iodide. The reason for this interesting fact must, for the present, remain unexplained.

The results obtained by Jones for the molecular weight of cadmium iodide in acetone are given in table 21, and are shown graphically in figure 16. The formula weight is 364, while the molecular weight found in a 0.09 normal solution in acetone is 448. Considerable polymerization is thus indicated.

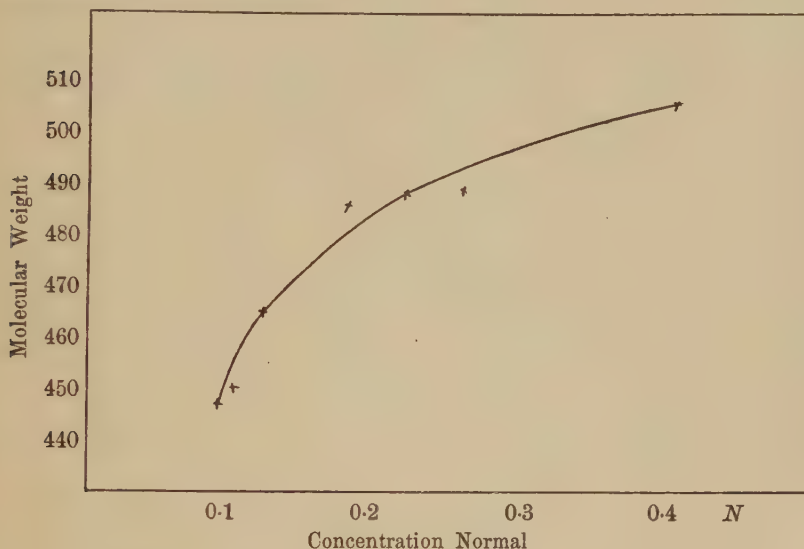


Fig. 16. Molecular Weight of Cadmium Iodide in Acetone.

Table 21.

Molecular Weight of Cadmium Iodide in Acetone.

Acetone Grams	CdI_2 Grams	Conc. Normal	B. P. Rise Degrees	Molecular Weight
55.16	1.7789	0.09	0.124	448.6
56.03	2.0540	0.10	0.140	451.7
57.51	2.4951	0.12	0.160	467.8
56.37	3.7790	0.18	0.236	490.1
55.92	4.5020	0.22	0.282	492.4
57.28	5.4000	0.26	0.330	492.9
57.28	8.5460	0.41	0.504	510.7

Summary.

The work of others has shown that the general law which correlates conductivity and viscosity fails in the case of lithium nitrate, lithium bromide, cobalt chloride, and calcium nitrate, when dissolved in mixtures containing acetone as one of the components of a binary solvent mixture.

This is made evident by the abnormally low values for conductivity of these substances in acetone, and it was thought that it might be due to association of the salt in acetone. Determination of conductivity at high dilutions has shown that lithium nitrate, when completely dissociated, is no exception to the rule that molecular conductivity varies inversely as the viscosity; and boiling-point measurements have shown that, at ordinary concentrations, the salt is associated in acetone to a considerable extent.

Cadmium iodide had already been shown to be associated in acetone, and further work on its conductivity in mixed solvents has shown that its behavior is similar to that of lithium nitrate.

The temperature coefficients of conductivity of lithium nitrate are of about the same order of magnitude as the temperature coefficients of fluidity, though generally somewhat smaller, except at high dilutions. This might be expected from the fact that dissociation is less at 25° than at 0°. This influence of temperature is seen more clearly in acetone solutions of cadmium iodide, which have negative temperature coefficients of conductivity below a dilution of 0.0001 normal.

Similar investigations are in progress, having to do with solutions of the other salts mentioned above.

Conductivity and Viscosity in Ternary Mixtures of Solvents.

A large amount of work has been performed with the object of learning something of the electrochemistry of organic solvents and of binary mixtures of these with each other. This is especially true with regard to the relations existing between conductivity and viscosity of solutions in such solvents. A full account of the work which has been done in this laboratory has been published as a monograph by Jones¹⁾, and the electrochemistry of nonaqueous solvents has been extensively discussed by Carrara²⁾.

The dependence of conductivity upon viscosity has been treated in the preceding section, and a brief summary of the more important work on binary mixtures has been given. In the following pages are recorded the results of a few preliminary experiments, which were made with the object of determining whether any essentially new principles were to be discovered by increasing the number of components of a solvent mixture from two to three. It would be, of course, impossible to predict whether or not the mutual action of three solvents upon each other would be the average action of the three possible pairs of

¹⁾ Carnegie Institution Pub. No. 80 (1907).

²⁾ Ahrens' Sammlung 12, No. 11 (1908).

components. No extensive study of this matter has, as yet, been made. We have measured the viscosity of ternary mixtures of water, methyl alcohol, ethyl alcohol and acetone, and the conductivity of lithium nitrate in these mixtures. The materials, apparatus and methods of making measurements were essentially the same as outlined in the preceding section. The following example will serve to indicate the method of designating the solvent mixtures: "Acetone (75% Methyl Alcohol and Water)" indicates a mixture of solvents made by adding stated amounts (percent by volume) of acetone to a mixture of methyl alcohol and water which contains 75%, by volume, of methyl alcohol.

Table 22.

Conductivity of Lithium Nitrate in Acetone (25% Methyl Alcohol and Water).
At 0°.

V	% Acetone.				
	0%	25%	50%	75%	100%
10	27.26	23.08	23.13	25.80	9.67
50	29.41	24.50	26.60	33.10	14.07
100	30.11	26.07	27.37	35.50	18.1
200	31.06	—	—	38.22	23.8
400	31.35	30.18	28.91	40.54	30.6
800	31.62	31.85	29.27	42.03	43.4
1600	32.16	—	29.73	43.21	55.3

At 25°.

10	56.46	48.07	44.78	40.31	10.87
50	61.51	51.65	51.89	55.29	15.64
100	63.53	55.43	53.88	59.78	19.5
200	65.72	—	—	64.80	25.3
400	66.41	64.05	57.42	68.85	32.4
800	66.94	66.63	58.21	71.78	45.5
1600	68.20	—	58.40	73.16	59.8

Table 23.

Conductivity of Lithium Nitrate in Acetone (50% Methyl Alcohol and Water).
At 0°.

V	% Acetone.				
	0%	25%	50%	75%	100%
10	21.86	22.54	25.15	28.09	9.67
50	23.91	25.55	29.57	37.62	14.07
100	24.79	26.57	31.08	41.25	18.1
200	25.37	27.11	32.55	44.28	23.8
400	25.47	28.70	34.14	47.31	30.6
800	26.10	28.62	34.17	48.52	43.4
1600	26.94	30.26	35.35	50.40	55.3

At 25°.

10	44.58	43.79	44.42	42.77	10.87
50	49.41	50.18	53.11	58.37	15.64

V	0 %	25 %	50 %	75 %	100 %
100	51.44	52.32	55.90	64.40	19.5
200	52.79	53.67	59.02	69.82	25.3
400	53.10	55.05	62.03	74.56	32.4
800	54.32	56.50	64.35	77.97	45.5
1600	56.50	57.95	64.41	80.10	59.8

Table 24.

Conductivity of Lithium Nitrate in Acetone (75% Methyl Alcohol and Water).

At 0°.

% Acetone.

V	0 %	25 %	50 %	75 %	100 %
10	24.16	26.32	29.56	31.55	9.67
50	27.56	30.99	36.94	44.86	14.07
100	28.67	32.99	38.90	50.16	18.1
200	29.60	34.11	41.90	55.20	23.8
400	29.82	34.75	42.96	58.80	30.6
800	30.62	35.30	44.31	61.75	43.4
1600	31.45	36.71	45.45	64.84	55.3

At 25°.

10	43.06	44.63	46.21	43.16	10.87
50	49.58	53.29	58.56	63.32	15.64
100	51.96	56.06	62.36	71.28	19.5
200	53.80	59.20	67.37	79.26	25.3
400	54.63	60.23	69.32	84.82	32.4
800	55.72	61.24	71.51	89.78	45.5
1600	58.06	63.88	73.49	94.22	59.8

Table 25.

Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Methyl Alcohol and Water.

% Acetone.

V	0 %	25 %	50 %	75 %	100 %
In Acetone (75 % Methyl Alcohol and Water).					
10	0.0428	0.0433	0.0374	0.0225	0.0049
50	0.0437	0.0443	0.0380	0.0268	0.0045
100	0.0444	0.0450	0.0387	0.0273	0.0031
200	0.0446	—	—	0.0278	0.0025
400	0.0447	0.0449	0.0394	0.0279	0.0023
800	0.0447	0.0437	0.0395	0.0283	0.0019
1600	0.0448	—	0.0386	0.0277	0.0032
In Acetone (50 % Methyl Alcohol and Water).					
10	0.0416	0.0377	0.0314	0.0209	See Above
50	0.0427	0.0385	0.0318	0.0221	„
100	0.0430	0.0388	0.0319	0.0224	„
200	0.0432	0.0391	0.0325	0.0231	„

V	0 %	25 %	50 %	75 %	100 %
400	0.0434	0.0367	0.0327	0.0230	See Above
800	0.0433	0.0390	0.0326	0.0243	"
1600	0.0439	0.0366	0.0326	0.0236	"

In Acetone (75 % Methyl Alcohol and Water).

V	0 %	25 %	50 %	75 %	100 %
10	0.0313	0.0278	0.0225	0.0151	See Above
50	0.0320	0.0288	0.0234	0.0165	"
100	0.0325	0.0290	0.0241	0.0168	"
200	0.0327	0.0294	0.0243	0.0174	"
400	0.0333	0.0292	0.0245	0.0177	"
800	0.0328	0.0294	0.0246	0.0182	"
1600	0.0338	0.0296	0.0247	0.0181	"

Table 26.

Conductivity of Lithium Nitrate in Acetone (25 % Ethyl Alcohol and Water).

At 0°.

% Acetone.

V	0 %	25 %	50 %	75 %	100 %
10	19.66	18.74	20.71	23.93	9.67
50	21.03	20.44	23.64	30.73	14.07
100	21.51	21.05	24.61	33.31	18.1
200	22.03	21.70	25.46	35.20	23.8
400	22.20	22.15	25.78	36.74	30.6
800	22.48	22.04	26.38	37.96	43.4
1600	24.54	22.83	26.69	40.74	55.3

At 25°.

V	0 %	25 %	50 %	75 %	100 %
10	46.70	42.51	41.31	39.75	10.87
50	51.11	47.25	47.93	52.10	15.64
100	52.37	48.76	50.12	56.84	19.5
200	54.00	50.42	52.19	60.51	25.3
400	54.60	51.76	52.93	63.21	32.4
800	55.39	51.62	54.17	65.59	45.5
1600	58.59	52.96	54.78	70.11	59.8

Table 27.

Conductivity of Lithium Nitrate in Acetone (50 % Ethyl Alcohol and Water).

At 0°.

% Acetone.

V	0 %	25 %	50 %	75 %	100 %
10	12.53	15.98	19.85	23.80	9.67
50	13.57	17.89	23.62	32.49	14.07
100	14.02	18.63	25.13	35.90	18.1
200	14.42	19.21	26.13	38.84	23.8
400	14.60	—	26.98	39.67	30.6
800	14.88	19.33	—	43.56	43.4
1600	14.88	20.56	30.23	46.13	55.3

V	0 %	At 25°.		% Acetone.	
		25 %	50 %	75 %	100 %
10	31.82	34.54	36.95	36.77	10.87
50	35.34	39.43	44.64	51.27	15.64
100	36.56	41.23	47.69	53.06	19.5
200	37.88	42.64	49.88	62.36	25.3
400	38.31	—	51.71	63.83	32.4
800	38.96	44.15	—	68.75	45.5
1600	39.35	45.56	53.86	71.67	59.8

Table 28.

Conductivity of Lithium Nitrate in Acetone (75 % Ethyl Alcohol and Water).

V	0 %	At 0°.		% Acetone.	
		25 %	50 %	75 %	100 %
10	12.01	15.84	20.41	23.29	9.67
50	13.80	19.00	26.84	35.29	14.07
100	14.48	20.21	29.06	40.41	18.1
200	15.14	20.92	31.76	44.80	23.8
400	15.41	21.67	32.70	48.43	30.6
800	15.76	21.52	33.55	51.38	43.4
1600	16.10	22.56	35.20	54.01	55.3

V	0 %	At 25°.		% Acetone.	
		25 %	50 %	75 %	100 %
10	25.56	29.66	33.32	32.59	10.87
50	29.91	36.32	44.69	50.39	15.64
100	31.64	38.85	48.68	58.35	19.5
200	33.12	40.44	53.90	65.72	25.3
400	33.90	42.11	55.52	71.59	32.4
800	34.88	41.91	57.32	76.39	45.5
1600	35.85	43.97	60.54	81.28	59.8

Table 29.

Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Acetone, Ethyl Alcohol and Water.

	% Acetone.				
V	0 %	25 %	50 %	75 %	100 %
	In Acetone (25 % Ethyl Alcohol and Water).				
10	0.0550	0.0507	0.0398	0.0265	0.0049
50	0.0572	0.0524	0.0411	0.0291	0.0045
100	0.0574	0.0526	0.0414	0.0282	0.0031
200	0.0581	0.0530	0.0420	0.0287	0.0025
400	0.0584	0.0535	0.0421	0.0288	0.0023
800	0.0585	0.0537	0.0422	0.0290	0.0019
1600	0.0555	0.0528	0.0421	0.0288	0.0032
	In Acetone (50 % Ethyl Alcohol and Water).				
10	0.0614	0.0464	0.0341	0.0218	See Above
50	0.0642	0.0482	0.0356	0.0231	"
100	0.0643	0.0485	0.0359	0.0247	"

V	0 %	25 %	%	75 %	100 %
200	0.0650	0.0488	0.0364	0.0242	See Above
400	0.0649	—	0.0367	0.0244	"
800	0.0647	0.0491	—	0.0231	"
1600	0.0658	0.0486	0.0313	0.0222	"

In Acetone (75 % Ethyl Alcohol and Water).

10	0.0451	0.0349	0.0253	0.0160	See Above
50	0.0467	0.0365	0.0267	0.0171	"
100	0.0474	0.0369	0.0270	0.0177	"
200	0.0475	0.0373	0.0278	0.0187	"
400	0.0480	0.0377	0.0278	0.0192	"
800	0.0485	0.0380	0.0283	0.0194	"
1600	0.0491	0.0379	0.0288	0.0202	"

Table 30.

Conductivity of Lithium Nitrate in Methyl Alcohol (25 % Ethyl Alcohol and Water).

At 0°.

% CH_3OH .

V	0 %	25 %	50 %	75 %	100 %
10	19.66	17.76	19.50	24.35	37.62
50	21.03	19.11	21.65	28.13	48.31
100	21.51	19.89	22.46	29.68	52.0
200	22.03	20.19	22.76	31.76	55.1
400	22.20	20.57	23.08	31.32	56.8
800	22.48	20.63	23.39	32.19	59.6
1600	24.54	21.09	23.34	32.73	61.9

At 25°.

10	46.70	40.13	39.04	41.67	51.31
50	51.11	44.13	44.05	48.85	67.2
100	52.37	45.97	45.81	51.49	72.6
200	54.00	46.48	46.53	53.73	76.8
400	54.60	47.86	47.35	53.94	80.0
800	55.39	48.10	47.96	56.14	83.7
1600	58.59	49.72	47.92	57.59	86.7

Table 31.

Conductivity of Lithium Nitrate in Methyl Alcohol (50 % Ethyl Alcohol and Water).

At 0°.

% CH_3OH .

V	0 %	25 %	50 %	75 %	100 %
10	12.53	15.35	19.19	25.18	37.62
50	13.57	16.96	21.95	30.04	48.31
100	14.02	17.61	22.87	31.69	52.0
200	14.42	18.02	23.75	32.97	55.1
400	14.60	18.41	24.61	34.18	56.8
800	14.88	18.60	24.98	34.57	59.6
1600	14.88	19.50	25.15	35.48	61.9

At 25°.					
% CH_3OH .					
V	0 %	25 %	50 %	75 %	100 %
10	31.82	33.24	36.13	41.18	51.31
50	35.34	37.35	41.91	49.48	67.2
100	36.56	39.10	43.87	52.36	72.6
200	37.88	40.08	45.72	54.91	76.8
400	38.31	41.57	47.44	57.06	80.0
800	38.96	41.63	48.06	57.67	83.7
1600	39.35	43.82	48.53	59.61	86.7

Table 32.

Conductivity of Lithium Nitrate in Methyl Alcohol (75 % Ethyl Alcohol and Water).

At 0°.					
% CH_3OH .					
V	0 %	25 %	50 %	75 %	100 %
10	12.01	15.46	20.00	26.46	37.62
50	13.80	17.96	23.82	32.38	48.31
100	14.48	19.03	25.22	34.69	52.0
200	15.14	19.72	26.11	36.17	55.1
400	15.41	20.32	26.77	37.46	56.8
800	15.76	20.55	27.15	38.51	59.6
1600	16.10	20.82	27.54	39.55	61.9

At 25°.					
V	0 %	25 %	50 %	75 %	100 %
10	25.56	29.28	34.09	40.91	51.31
50	29.91	34.77	41.20	50.50	67.2
100	31.64	36.93	43.89	54.35	72.6
200	33.12	38.41	45.52	56.89	76.8
400	33.90	39.81	46.82	59.08	80.0
800	34.88	40.52	47.51	60.86	83.7
1600	35.85	41.34	48.39	62.84	86.7

Table 33.

Temperature Coefficients of Conductivity of Lithium Nitrate in Mixtures of Methyl Alcohol, Ethyl Alcohol and Water.

% CH_3OH .					
V	0 %	25 %	50 %	75 %	100 %
In Methyl Alcohol (25 % Ethyl Alcohol and Water).					
10	0.0550	0.0504	0.0400	0.0284	0.0145
50	0.0572	0.0524	0.0414	0.0295	0.0157
100	0.0574	0.0524	0.0415	0.0294	0.0155
200	0.0581	0.0521	0.0417	0.0276	0.0147
400	0.0584	0.0530	0.0420	0.0289	0.0172
800	0.0585	0.0532	0.0420	0.0298	0.0162
1600	0.0555	0.0542	0.0422	0.0301	0.0160

In Methyl Alcohol (50 % Ethyl Alcohol and Water).

10	0.0614	0.0466	0.0353	0.0254	See Above
50	0.0642	0.0481	0.0364	0.0258	„

V	0 %	25 %	50 %	75 %	100 %
100	0.0643	0.0488	0.0367	0.0262	See Above
200	0.0650	0.0492	0.0370	0.0266	"
400	0.0649	0.0503	0.0371	0.0267	"
800	0.0647	0.0495	0.0365	0.0267	"
1600	0.0658	0.0499	0.0372	0.0272	"

In Methyl Alcohol (75 % Ethyl Alcohol and Water).

10	0.0451	0.0358	0.0282	0.0219	See Above
50	0.0467	0.0374	0.0292	0.0224	"
100	0.0474	0.0376	0.0297	0.0227	"
200	0.0475	0.0379	0.0297	0.0229	"
400	0.0480	0.0383	0.0300	0.0231	"
800	0.0485	0.0388	0.0300	0.0232	"
1600	0.0491	0.0394	0.0303	0.0235	"

Table 34.

Viscosity and Fluidity of Mixtures of Acetone, Methyl Alcohol and Water.

% Acetone	η 0°	η 25°	Φ 0°	Φ 25°	Temp. Coef.
Acetone (25 % Methyl Alcohol and Water).					
0	0.03286	0.01368	30.44	73.11	0.0561
25	0.03386	0.01428	29.53	70.04	0.0549
50	0.02597	0.01209	38.50	82.75	0.0460
75	0.01310	0.00751	76.36	133.22	0.0303
100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (50 % Methyl Alcohol and Water).					
0	0.03586	0.01541	27.81	64.89	0.0531
25	0.02850	0.01340	35.09	74.65	0.0451
50	0.01926	0.01514	51.92	99.96	0.0371
75	0.00984	0.00620	101.63	161.40	0.0235
100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (75 % Methyl Alcohol and Water).					
0	0.02461	0.01253	41.64	79.84	0.0463
25	0.01824	0.00990	54.81	101.06	0.0338
50	0.01203	0.00726	83.10	137.79	0.0263
75	0.00705	0.00491	141.76	203.85	0.0175
100	0.00429	0.00346	233.21	288.95	0.0096

Table 35.

Viscosity and Fluidity of Mixtures of Acetone, Ethyl Alcohol and Water.

% Acetone	η 0°	η 25°	Φ 0°	Φ 25°	Temp. Coef.
Acetone (25 % Ethyl Alcohol and Water).					
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04329	0.01644	23.10	60.83	0.0653
50	0.02856	0.01288	35.02	77.63	0.0487
75	0.01356	0.00770	73.74	129.88	0.0305
100	0.00429	0.00346	233.21	288.95	0.0096

% Acetone	η 0°	η 25°	Φ 0°	Φ 25°	Temp. Coef.
Acetone (50 % Ethyl Alcohol and Water).					
0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04152	0.01693	24.09	79.05	0.0580
50	0.02284	0.01123	43.78	89.05	0.0414
75	0.01047	0.00648	95.54	154.41	0.0246
100	0.00429	0.00346	233.21	288.95	0.0096
Acetone (75 % Ethyl Alcohol and Water).					
0	0.04826	0.01983	20.72	50.41	0.0573
25	0.02807	0.01341	35.63	74.56	0.0437
50	0.01529	0.00853	65.41	117.21	0.0317
75	0.00935	0.00637	106.93	156.87	0.0177
100	0.00429	0.00346	233.21	288.95	0.0096

Table 36.

Viscosity and Fluidity of Mixtures of Methyl Alcohol, Ethyl Alcohol and Water.

% Acetone	η 0°	η 25°	Φ 0°	Φ 25°	Temp. Coef.
Methyl Alcohol (25 % Ethyl Alcohol and Water).					
0	0.05111	0.01745	19.57	57.30	0.0770
25	0.04851	0.01862	20.61	53.70	0.0642
50	0.03804	0.01702	26.29	58.76	0.0493
75	0.02198	0.01160	45.49	86.24	0.0358
100	0.00857	0.00583	116.71	171.60	0.0176
Methyl Alcohol (50 % Ethyl Alcohol and Water).					
0	0.06949	0.02298	14.39	43.51	0.0643
25	0.04919	0.01994	20.33	50.14	0.0587
50	0.03086	0.01481	32.41	67.52	0.0433
75	0.01928	0.01083	51.88	92.34	0.0311
100	0.00857	0.00583	116.71	171.60	0.0176
Methyl Alcohol (75 % Ethyl Alcohol and Water).					
0	0.04826	0.01983	20.72	50.41	0.0573
25	0.03468	0.01614	28.83	61.97	0.0461
50	0.02337	0.01216	42.86	82.23	0.0369
75	0.01477	0.00880	67.70	113.62	0.0271
100	0.00857	0.00583	116.71	171.60	0.0176

From the results thus far obtained, it would seem that the viscosity and conductivity values in ternary mixtures are about what might be expected from a knowledge of the behavior of solutions in binary solvent mixtures. A series of experiments with a salt, such as potassium iodide, which shows no abnormality in any of the single solvents, would make possible a more exact comparison of experimental with calculated values. More extensive work along these lines will be taken up in this laboratory in the near future, as well as further investigations in binary mixtures.

BIOGRAPHY.

The author of this dissertation, Edward G. Mabin, was born near La Fayette, Indiana, on August 16, 1876. He entered Valparaiso College in 1897, and Purdue University in 1898. From Purdue University he received the degree of Bachelor of Science in 1901, and that of Master of Science in 1903. In his senior year he was Student-Assistant in Chemistry and he held the position of Instructor in Chemistry from 1902 until 1906, when he entered the Johns Hopkins University as a graduate student in chemistry, where in 1907 he was appointed Fellow in Chemistry. His principal subject was chemistry, and his subordinate subjects were physical chemistry and mathematics.
